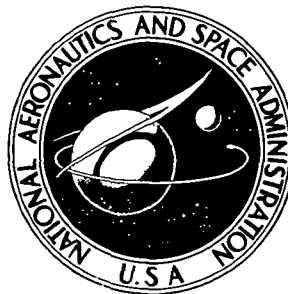


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**INFRARED EMISSION  
FROM THE ATMOSPHERE  
ABOVE 200 KM**

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16 Abstract  <p>Many of the atoms and molecules of the earth's atmosphere radiate in the infrared. This radiation is calculated from <math>4\mu</math> to <math>1000\mu</math> for altitudes between 200 km and 400 km; only zenith lines of sight are considered. The excitation of the atoms and molecules is due to collisions with other molecules, and to absorption of radiation from the earth and sun. In some cases the abundances of the molecules had to be estimated. The most important lines are the forbidden lines from atomic oxygen at <math>63.1\mu</math> and <math>147\mu</math>, and the vibration-rotation band of nitric oxide at <math>5.3\mu</math>. These lines can have intensities as high as a few times <math>10^{-3}</math> ergs <math>\text{cm}^{-2}</math> <math>\text{sec}^{-1}</math> <math>\text{sr}^{-1}</math> at 200 km altitude. In addition, the vibration-rotation bands of <math>\text{NO}^+</math> at <math>4.3\mu</math> and CO at <math>4.7\mu</math> and the pure rotation lines of NO and <math>\text{NO}^+</math> could be detected by infrared telescopes in space.</p>					
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# INFRARED EMISSION FROM THE ATMOSPHERE ABOVE 200 KM

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## SUMMARY

Many of the atoms and molecules of the earth's atmosphere radiate in the infrared. This radiation is calculated from  $4\mu$  to  $1000\mu$  for altitudes between 200 km and 400 km; only zenith lines of sight are considered. The excitation of the atoms and molecules is due to collisions with other molecules, and to absorption of radiation from the earth and sun. In some cases the abundances of the molecules had to be estimated. The most important lines are the forbidden lines from atomic oxygen at  $63.1\mu$  and  $147\mu$ , and the vibration-rotation band of nitric oxide at  $5.3\mu$ . These lines can have intensities as high as a few times  $10^{-3}$  ergs  $\text{cm}^{-2}$   $\text{sec}^{-1}$   $\text{sr}^{-1}$  at 200 km altitude. In addition, the vibration-rotation bands of  $\text{NO}^+$  at  $4.3\mu$  and CO at  $4.7\mu$  and the pure rotation lines of NO and  $\text{NO}^+$  could be detected by infrared telescopes in space.

## INTRODUCTION

Infrared telescopes on space satellites will have to look through the tenuous gas of the earth's outer atmosphere. This gas itself radiates in the infrared, and the radiation from the gas will enter the detectors of the telescope along with the radiation from the stars, planets, and galaxies that are the goals of the observations. An attempt is made here to estimate the amounts of infrared radiation that will enter the shuttle- and satellite-based telescopes and their detectors from the overlying natural atmosphere.

The gas that is left at this altitude is composed mainly of neutral O,  $\text{N}_2$ ,  $\text{O}_2$ , Ar, H, and He. Of these, H and He produce line radiation only through recombination from ionized H and He. The spectrum of Ar also contains no low excitation infrared lines.  $\text{N}_2$  and  $\text{O}_2$ , being homonuclear diatomic molecules, have no dipole moment and hence have no permitted rotational or vibration-rotational lines. However,  $\text{O}_2$  has two unpaired electrons (ground state  $^3\Sigma$ ) and hence has a forbidden magnetic dipole rotation spectrum. Neutral atomic oxygen has very strong forbidden transitions among the fine structure levels of its  $^3\text{P}$  ground term. In addition, there should be neutral species with abundances too small to detect; these species have diffused upwards from the lower atmosphere. There are no low excitation infrared lines of neutral N, but NO, CO, and  $\text{CO}_2$  have strong vibration-rotation bands in the infrared. Their abundances will have to be estimated.

Ultraviolet photons from the sun can ionize any of the neutral atoms and molecules just mentioned. Charge exchange reactions also affect the abundances

of the ions. From the UV flux from the sun and the known abundance of neutrals, it should be possible to calculate the abundance of ions and minor constituents. However, many reactions are involved and the cross sections and diffusion rates are often known poorly, if at all. Fortunately, measurements have been made of the abundances of the ionic species under close to average conditions.

## THE ATMOSPHERE ABOVE 200 KM

The atmosphere above 200 km is thought to be in diffusive equilibrium for most constituents. Numerical models, such as those described in CIRA 1972 (ref. 1), must be used to obtain the density of the atmosphere which is strongly dependent on the kinetic gas temperature at these altitudes. The main differences between the models in CIRA 1972 and those in the U.S. Standard Atmosphere Supplements, 1966 (ref. 2) is that the former models contain more neutral oxygen and less  $O_2$  and  $N_2$  to conform better to observations at 150 km. Consequently, the temperature required to produce a given density is also different. The tables in CIRA 1972 give the density of each component as a function of altitude for exospheric temperatures ranging from  $500^\circ\text{K}$  to  $2200^\circ\text{K}$ . The temperature of the atmosphere increases very rapidly from  $210\text{--}270^\circ\text{K}$  at 100 km to the final exospheric temperature. At 350 km the temperature is only about 3 percent less than the exospheric temperature.

The models in the tables are static models; they do not take into account the dynamical variation of temperature and density of the atmosphere. The main temperature variations are due to the solar cycle, short-term changes in the active regions on the sun, and the daily variation due to the rotation of the earth, and the geomagnetic activity. Given the parameters for the solar and geomagnetic activity and the time of day and latitude on earth, CIRA 1972 (ref. 1) gives formulas for computing the appropriate exospheric temperature. The mean exospheric temperature is found to be about  $1000^\circ\text{K}$ ; the temperature is less than  $550^\circ\text{K}$  for only 1 percent of the time and greater than  $1900^\circ\text{K}$  for only 1 percent of the time. The daytime temperature is higher by a factor of 1.3 than the nighttime temperature for the same solar flux. Over a solar cycle, the number of days with each value of the exospheric temperature forms a distribution function that is double peaked if the daytime and nighttime temperatures are considered separately. The two peaks correspond to solar minimum and solar maximum. Nicolet (ref. 3) investigated the temperatures for the solar cycle that had its maximum in 1957-1958. For this cycle, the peaks of the distribution function occurred at about  $900^\circ\text{K}$  and  $1500^\circ\text{K}$  for daytime temperatures and  $700^\circ\text{K}$  and  $1200^\circ\text{K}$  for nighttime temperatures. It is now apparent that the peak temperatures of the last solar maximum were several hundred degrees lower and that the 1957-58 maximum was exceptionally high. Because of the day-night variation, a satellite will see the temperature vary by up to 30 percent (depending on angular distance to the point of temperature maximum) every half orbit and the density vary by up to a factor of two.

(For diffusive equilibrium, the density  $N(R)$  goes as  $\exp(-R/H)$  where the scale height,  $H$ , equals  $kT/mg$ ,  $k$  is the Boltzmann constant,  $T$  is the kinetic

gas temperature,  $m$  is the mass of the constituent,  $g$  is the acceleration of gravity, and  $R$  is the altitude. If the temperature is constant, one can integrate  $N(R)$  to get the column density  $= N_0 H \exp[-(R - R_0)/H]$  where  $N_0$  is the density at  $R_0$ . Then the change in column density with temperature is

$$\frac{\Delta \text{ col. den. }}{\text{ col. den. }} = \frac{\Delta T}{T} \left[ 1 + (R - R_0)mg/kT \right]$$

where  $R_0$  is the height at which the density is constant, about 90-120 km. Of course the temperature is not constant down to  $R_0 = 120$  km, but the above expression gives the correct dependences on  $R$ ,  $m$ , and  $T$ .)

In addition to the density variations due to temperature, there is a semiannual density variation of unknown cause: the density can vary by up to 15 percent from the densities in the tables for a given temperature at an altitude of 350 km. The maximum variation is over 50 percent at 800 km. Again, CIRA 1972 (ref. 1) gives formulas and tables for computing these variations.

All the formulas for the temperature and density variations represent fits to the observed data. For any particular day they may be considerably off, but on the average they should be as accurate as the data. Since there is so much variation in the temperature and density of the upper atmosphere, it is impossible to follow the atmosphere through one cycle of a satellite's orbit until after the satellite has been flying, when the required parameters of the average solar flux, solar activity, and geomagnetic activity are known. In order to get representative values of the infrared radiation, three temperatures were chosen for this computation: the average 1000° K and the extremes 550° K and 2000° K. The densities corresponding to these temperatures were used to compute average and extreme radiation from neutral O and O<sub>2</sub>. The information on ions and neutral NO corresponds to the temperatures not far different from the average 1000° K.

## INFRARED RADIATION

The specific intensity in a line or band  $I$  is given by

$$I(R) = \int_0^\infty d\nu \int_R^\infty \frac{h\nu}{4\pi} A_{ul} \phi_\nu N_u \exp\left(\frac{h\nu}{4\pi} \phi_\nu \int_r^R B_{ul} N_u - B_{lu} N_l dr\right) dr$$

where  $\nu$  is the frequency,  $h$  is the Planck constant,  $A_{ul}$ ,  $B_{ul}$ , and  $B_{lu}$  are Einstein coefficients,  $N_u/N_{\text{total}}$  and  $N_l/N_{\text{total}}$  are the fractions of atoms or molecules in the upper and lower levels respectively, and  $\phi_\nu$  is the normalized line profile function.  $N_{\text{total}}$  is the number density of a particular species of atom or molecule. Above 200 km, the lines are optically thin and  $I$  is approximated by

$$I(R) = \int_R^\infty \frac{h\nu}{4\pi} A_{ul} N_u dr$$

which becomes

$$I(R) = \frac{h\nu}{4\pi} A_{ul} N_u / N_{\text{total}} \times (\text{col. den.})$$

if the excitation is constant with altitude  $R$ . Col. den. is the column density  $\int_R^\infty N_{\text{total}} dr$  in atoms or molecules/cm<sup>2</sup>.

The intensity  $I$  will usually be expressed in ergs cm<sup>-2</sup> sec<sup>-1</sup> sr<sup>-1</sup>. It is converted to W cm<sup>-2</sup> sr<sup>-1</sup> by multiplying by 10<sup>-7</sup>. Wavelengths are given in microns,  $\mu$ . The results of the calculations for each molecule and line will be plotted in figures 1(a)-(e).

### Neutral Atomic Oxygen

The ground state of neutral oxygen is a <sup>3</sup>P triplet of the 2p<sup>4</sup> configuration. Fine structure transitions within the ground state produce forbidden lines in the far infrared at 63.1 $\mu$  (<sup>3</sup>P<sub>2</sub> - <sup>3</sup>P<sub>1</sub>) and 147 $\mu$  (<sup>3</sup>P<sub>1</sub> - <sup>3</sup>P<sub>0</sub>). The familiar optical forbidden lines of neutral oxygen are at 5577 Å (<sup>1</sup>D<sub>2</sub> - <sup>1</sup>S<sub>0</sub>) and 6300 Å (<sup>3</sup>P<sub>2</sub> - <sup>1</sup>D<sub>2</sub>). The upper levels are excited and deexcited by collisions and radiation. The equilibrium populations are given by the Boltzmann equation  $N_2/N_1 = g_2/g_1 \exp[-(E_2 - E_1)/kT_{\text{ex}}]$  where  $T_{\text{ex}}$  is defined by this equation and  $g_1$  and  $g_2$  are the statistical weights of levels one and two, respectively. If  $T_{\text{ex}}$  is the same as the translational temperature of the neutral gas,  $T$ , the populations are in local thermodynamic equilibrium (LTE). Saraph (ref. 4) has given cross sections for collisional excitation by electrons. Calculations with the observed electron densities show that the level populations are within 90 percent of the LTE population at 350 km and within 80 percent at 500 km for  $T = 1000^\circ$  K for excitation by electrons alone. Collisions with neutral atoms and molecules will increase the populations of the upper levels. In fact, the populations of the upper levels could be greater than the LTE populations, because the electron temperature is substantially higher than the gas temperature. (At 550° K, the populations may be less than the LTE populations because the gas density is so small). For the calculations below, it was assumed that the upper levels are populated according to the Boltzmann equation at the temperature of the neutral gas because the density of the neutrals is two to three orders of magnitude greater than the electron density. In any event, the LTE populations do not vary greatly for the temperatures under consideration (see table 1).

TABLE 1.— LTE POPULATIONS FOR THE <sup>3</sup>P GROUND STATE OF NEUTRAL OXYGEN

$T, ^\circ\text{K}$	$N(^3P_0)/N_{\text{tot}}$	$N(^3P_1)/N_{\text{tot}}$	$N(^3P_2)/N_{\text{tot}}$
550	0.073	0.263	0.664
1000	.089	.294	.617
2000	.100	.314	.586
3000	.101	.335	.563



For the calculation of the [OI] line intensities, the number densities were taken from CIRA 1972 (ref. 1) and the Einstein coefficients from Garstang (ref. 5):  $A(^3P_1 - ^3P_0) = 1.7 \times 10^{-5} \text{ sec}^{-1}$  and  $A(^3P_2 - ^3P_1) = 9.0 \times 10^{-5} \text{ sec}^{-1}$ . The results are given in table 2. The optical depth in the line center  $\tau(\Delta\nu = 0)$  is given by

$$\tau_{63.1\mu}(\Delta\nu=0) = \frac{A_{63.1} \lambda^3}{8\pi(2\pi kT/m)^{1/2}} \frac{(3/5)N(^3P_2) - N(^3P_1)}{N_{\text{tot}}} \times \text{col. den.}$$

if there is no turbulent line broadening. These optical depths are so small at 300 km that self-absorption is negligible. However, at low altitudes the optical depth is large enough that self-absorption should be considered (Kockarts and Peetermanns, ref. 6).

The rocket observations of [OI] that have been made have all been for altitudes below 120 km (Feldman and McNutt, ref. 7).

TABLE 2.— LINE INTENSITIES FOR NEUTRAL OXYGEN

Altitude, km	Column density, $\text{cm}^{-2}$	$I$ , ergs $\text{cm}^{-2} \text{ sec}^{-1} \text{ sr}^{-1}$		$\tau_O$ , 63.1 $\mu$
		63.1 $\mu$	147 $\mu$	
$T = 550^\circ \text{ K}$				
400	$1.52 \times 10^{13}$	$9.0 \times 10^{-7}$	$2.0 \times 10^{-8}$	0.00001
350	$6.86 \times 10^{13}$	$4.1 \times 10^{-6}$	$9.2 \times 10^{-8}$	.00006
300	$3.22 \times 10^{14}$	$1.9 \times 10^{-5}$	$4.3 \times 10^{-7}$	.0003
250	$1.58 \times 10^{15}$	$9.4 \times 10^{-5}$	$2.1 \times 10^{-6}$	.001
200	$8.29 \times 10^{15}$	$4.9 \times 10^{-4}$	$1.1 \times 10^{-5}$	.008
$T = 1000^\circ \text{ K}$				
400	$7.97 \times 10^{14}$	$5.3 \times 10^{-5}$	$1.3 \times 10^{-6}$	.0003
350	$1.83 \times 10^{15}$	$1.2 \times 10^{-4}$	$3.0 \times 10^{-6}$	.0007
300	$4.30 \times 10^{15}$	$2.9 \times 10^{-4}$	$7.0 \times 10^{-6}$	.002
250	$1.05 \times 10^{16}$	$6.9 \times 10^{-4}$	$1.7 \times 10^{-5}$	.004
200	$2.72 \times 10^{16}$	$1.8 \times 10^{-3}$	$4.3 \times 10^{-5}$	.011
$T = 2000^\circ \text{ K}$				
400	$9.18 \times 10^{15}$	$6.5 \times 10^{-4}$	$1.7 \times 10^{-5}$	.001
350	$1.39 \times 10^{16}$	$9.8 \times 10^{-4}$	$2.5 \times 10^{-5}$	.002
300	$2.14 \times 10^{16}$	$1.5 \times 10^{-3}$	$3.9 \times 10^{-5}$	.003
250	$3.39 \times 10^{16}$	$2.4 \times 10^{-3}$	$6.1 \times 10^{-5}$	.005
200	$5.79 \times 10^{16}$	$4.0 \times 10^{-3}$	$1.0 \times 10^{-4}$	.011

## O<sub>2</sub> and N<sub>2</sub>

The homonuclear diatomic molecule, O<sub>2</sub>, has no electric dipole moment. Thus the electric dipole vibration-rotation and rotational spectra are strictly forbidden. However, there are two unpaired electrons in O<sub>2</sub>, giving a ground state of <sup>3</sup>Σ and a magnetic dipole moment. The resulting magnetic dipole rotational spectrum has been observed and discussed by Gebbie *et al.* (ref. 8). These lines have also been observed in the solar absorption spectrum. Gebbie *et al.* give theoretical and observed values for the integrated line strengths  $S = \int \kappa \, d\nu$  where  $\kappa = d\tau/dr$ . The integrated line strength is proportional to the Einstein A coefficient times the population of the lower energy level. For the strongest lines between 165μ and 705μ, the maximum theoretical values of A are of the order of 10<sup>-7</sup> sec<sup>-1</sup>; the observed values agree within 25 percent. The observed values of A were used and A = 10<sup>-7</sup> sec<sup>-1</sup> was assumed for transitions between the unobserved higher rotational levels. The molecule O<sub>2</sub> is described by Hund's case b; the observations of Gebbie *et al.* only cover wavelengths with transitions as high as quantum change ΔK = 11 - 9, but rotational energy levels were calculated to K = 27. The population of a level is given by

$$\frac{N(J,K)}{N_{\text{tot}}} = \frac{(2J+1) \exp[-K(K+1)hcB/kT]}{3kT/2hcB}$$

if the energy levels are functions of K only (actually there is a small splitting with J). The rotational constant is B (McKnight and Gordy, ref. 9) and J = K - 1, K, or K + 1. For T = 300° K, the maximum population occurs at K = 7, J = 8, but for T = 1000° K the maximum population is at K = 15 - 17, and for T = 2000° K for the maximum is at K = 21 - 23. (Only odd numbered values of K are populated.) Therefore, at 1000° K estimates of the intensities for the strongest lines require extrapolation to get values for the Einstein A coefficients.

In table 3 the transition K = 23 - 21 is the strongest for T = 1000° K but K = 27 - 25 is strongest for T = 2000° K. Normally the Einstein A coefficients increase with decreasing wavelength; however the O<sub>2</sub> rotational spectrum becomes increasingly forbidden with increasing K (Gebbie *et al.*, ref. 8).

The above estimates for the Einstein A coefficients and the column densities from CIRA 1972 (ref. 1) were used to predict the intensities of the strongest O<sub>2</sub> rotational lines in table 4. These lines are much weaker than the lines from neutral oxygen.

The molecule N<sub>2</sub> has a much larger column density than O<sub>2</sub> (see table 4). However, since N<sub>2</sub> is a homonuclear molecule with no magnetic dipole moment due to electrons, its rotation and rotation-vibration spectrum are strongly forbidden. Because the nuclear spin of the nitrogen atom is one, there is a nuclear magnetic moment for N<sub>2</sub>. The transitions, if they existed, would have an extremely small transition probability because of the small nuclear magnetic moment; the intensities of any N<sub>2</sub> rotational lines would be much smaller than the intensities of O<sub>2</sub> rotational lines.

TABLE 3.— SOME ROTATIONAL LINES FOR O<sub>2</sub>

$\Delta K, \Delta J$ Transition	$\lambda_{\mu}$	$A, \text{sec}^{-1}$	$\frac{hcA}{4\pi\lambda} \frac{N_J}{N_{\text{tot}}}, \text{ergs sec}^{-1} \text{sr}^{-1}$	
			$T = 1000^{\circ} \text{K}$	$T = 2000^{\circ} \text{K}$
3-1, 2-2	705.8	$5.4 \times 10^{-8}$	$7.4 \times 10^{-26}$	$2.9 \times 10^{-26}$
5-3, 4-4	387.4	$6.3 \times 10^{-8}$	$2.7 \times 10^{-25}$	$1.0 \times 10^{-25}$
9-7, 8-8	204.4	$1.2 \times 10^{-7}$	$1.6 \times 10^{-24}$	$6.5 \times 10^{-25}$
11-9, 10-10	165.4	$9.2 \times 10^{-8}$	$1.7 \times 10^{-24}$	$7.6 \times 10^{-25}$
15-13, 14-14	120.5	$1.0 \times 10^{-7}$	$2.9 \times 10^{-24}$	$1.4 \times 10^{-24}$
19-17, 18-18	94.5	↓	$3.4 \times 10^{-24}$	$1.9 \times 10^{-24}$
23-21, 22-22	77.8		$3.6 \times 10^{-24}$	$2.4 \times 10^{-24}$
27-25, 24-24	66.1		$2.9 \times 10^{-24}$	$2.7 \times 10^{-24}$

TABLE 4.— INTENSITIES FOR ROTATIONAL LINES OF O<sub>2</sub>

Altitude, km	N <sub>2</sub> Column density, cm <sup>-2</sup>	O <sub>2</sub> Column density, cm <sup>-2</sup>	Intensity, ergs cm <sup>-2</sup> sec <sup>-1</sup> sr <sup>-1</sup>	
			77.8μ	66.1μ
T = 1000° K				
400	1.45×10 <sup>13</sup>	4.19×10 <sup>11</sup>	1.5×10 <sup>-12</sup>	1.4×10 <sup>-12</sup>
350	6.23×10 <sup>13</sup>	2.21×10 <sup>12</sup>	7.9×10 <sup>-12</sup>	7.1×10 <sup>-12</sup>
300	2.81×10 <sup>14</sup>	1.24×10 <sup>13</sup>	4.4×10 <sup>-11</sup>	4.0×10 <sup>-11</sup>
250	1.35×10 <sup>15</sup>	7.67×10 <sup>13</sup>	2.8×10 <sup>-10</sup>	2.5×10 <sup>-10</sup>
200	7.31×10 <sup>15</sup>	5.16×10 <sup>14</sup>	1.9×10 <sup>-9</sup>	1.7×10 <sup>-9</sup>
T = 2000° K				
400	1.01×10 <sup>15</sup>	5.28×10 <sup>13</sup>	1.3×10 <sup>-10</sup>	1.4×10 <sup>-10</sup>
350	2.10×10 <sup>15</sup>	1.23×10 <sup>14</sup>	3.0×10 <sup>-10</sup>	3.3×10 <sup>-10</sup>
300	4.52×10 <sup>15</sup>	2.94×10 <sup>14</sup>	7.2×10 <sup>-10</sup>	8.0×10 <sup>-10</sup>
250	1.03×10 <sup>16</sup>	7.52×10 <sup>14</sup>	1.8×10 <sup>-9</sup>	2.0×10 <sup>-9</sup>
200	2.66×10 <sup>16</sup>	2.24×10 <sup>15</sup>	5.5×10 <sup>-9</sup>	6.1×10 <sup>-9</sup>

## Nitric Oxide

Nitric oxide has not been observed in the earth's atmosphere at heights greater than about 150 km; calculations of the emission from NO must employ theoretical models and extrapolation. Ghosh (ref. 10) made a model for the NO abundance to 280 km; however, according to Strobel (ref. 11), Ghosh's reaction rates are in error. Strobel, Hunten, and McElroy (ref. 12) and Strobel (ref. 11) have also computed models for the NO abundance up to

240 km. The models of Strobel *et al.* are for an exospheric temperature of 750° K and a variety of assumptions about the reaction rates. Strobel (ref. 11) computed the daily variation for a minimum exospheric temperature of 940° K (that is, the maximum temperature in his model is ~1200° K).

Column densities were estimated from the models of Strobel *et al.* (ref. 12) and Strobel (ref. 11). The density of NO was first extrapolated from 240 km to infinity. Above 120 km, the number density of a molecule is generally determined by diffusive mixing, although chemical reactions are important for NO lower than about 250 km. For diffusive mixing,

$$N(R) = N_o \exp[-(R - R_o)/H]$$

where  $N_o$  is the density at  $R_o$ . Obviously, the scale height  $H(= kT/mg)$  is not constant with altitude. However, if  $H$  is constant, the equation for  $N$  can be integrated directly to get

$$\text{Col. den. } (R) = N_o H \exp[-(R - R_o)/H]$$

Values of  $H$  at  $R = 300$  km and 250 km are given in table 5.

TABLE 5.— SCALE HEIGHTS FOR DIFFUSIVE MIXING

Molecule	Scale height, km	
	$T = 1000^\circ \text{ K}$	$T = 750^\circ \text{ K}$
$R = 300 \begin{cases} \text{O}_2 \\ \text{NO} \\ \text{N}_2 \end{cases}$	29.26 31.21 33.44	21.95 23.41 25.08
$R = 250 \begin{cases} \text{O}_2 \\ \text{NO} \\ \text{N}_2 \end{cases}$	28.76 30.68 32.87	21.57 23.01 24.61

However, since the temperature, and thus the scale height, are variable with altitude, it is better to use the scale heights for  $\text{N}_2$  and  $\text{O}_2$  for a complete model, and take the average to get the scale height for NO (table 6). Since

TABLE 6.— SCALE HEIGHTS FOR NO

$T, ^\circ \text{K}$	$N_o (R_o = 230 \text{ km}), \text{ cm}^{-3}$	$H, \text{ km}$
750	$1.6 \times 10^6$	22.50
940	$2.0 \times 10^6$	28.82
1200	$6.0 \times 10^6$	36.79

Strobel (ref. 11) used models that are almost identical to the model in the U.S. Standard Atmosphere Supplements 1966 (ref. 2), scale heights from these models were used. Values of  $H$  and  $N_0$  were interpolated for  $T = 1000^\circ \text{ K}$  and the column density was computed. The column density for  $T = 1000^\circ \text{ K}$  is larger by a factor of 2 than the column density for  $T = 940^\circ \text{ K}$  at 350 km altitude.

The errors in the column densities may be very large because of uncertainties in the models and the method of extrapolation. The model by Ghosh (ref. 10) is an order of magnitude less dense in NO at 230 km than Strobel's (ref. 11) model. The column density at 85 km has been measured by Barth (ref. 13) to be  $1.7 \times 10^{14} \text{ cm}^{-2}$ . However, the column density for Strobel's (ref. 11) model at 85 km is greater than  $6 \times 10^{14} \text{ cm}^{-2}$ . Strobel compared his results with the observations of Meira (ref. 14) between 70 km and 115 km. The integrated column density is larger by a factor of 2 for Strobel's calculations, but the number densities at 100 km ( $10^8 \text{ cm}^{-3}$ ) agree "remarkably" well. Strobel noted that if the scale height for NO above 100 km were lower, the column densities would agree better, but then the density and column density at 250 km would be greatly lower. Strobel *et al.* (ref. 12) also compared their results to various observations from 85 km to 150 km. They concluded that the agreement is good. Rusch (ref. 15) also measured the density of NO to be  $\sim 10^8 \text{ cm}^{-3}$  at 105 km. Although atmospheric models vary greatly in density and temperature at high altitudes, such variation is very small around 100 km. Thus the discrepancy between the observed and theoretical NO densities cannot be ascribed to atmospheric variation.

The vibration-rotation bands lie at  $5.3\mu$  for the fundamental ( $\Delta v = 1$ ),  $2.7\mu$  for the first overtone ( $\Delta v = 2$ ), and  $1.8\mu$  for the second overtone ( $\Delta v = 3$ ). The wavelength can be considered to be constant for the band. The Einstein A coefficients are not measured directly; instead one measures the integrated absorption coefficient  $S = \int \kappa \, dv / Pc$ , where  $P$  is the pressure in atmospheres. For NO at STP, 0.999876 of the molecules are in the ground vibrational state and

$$S_{\Delta v=1} \propto B_{01}N_0 \propto A_{10}N_0 \text{ and } S_{\Delta v=2} \propto B_{02}N_0 \propto A_{20}N_0$$

that is,  $A = 2.8038 \times 10^{-8} S / \lambda^2 \text{ cm}^{-2} \text{ atm}^{-1}$ . The theoretical calculations of Michels (ref. 16) give  $S_{01} = 134 \text{ cm}^{-2} \text{ atm}^{-1}$  ( $A_{10} = 13.2 \text{ sec}^{-1}$ );  $S_{02} = 2.0 \text{ cm}^{-2} \text{ atm}^{-1}$  ( $A_{20} = 0.78 \text{ sec}^{-1}$ ); and  $S_{03} = 0.08 \text{ cm}^{-2} \text{ atm}^{-1}$  ( $A_{30} = 0.07 \text{ sec}^{-1}$ ). Measurements of  $S_{01}$  range from  $74 \text{ cm}^{-2} \text{ atm}^{-1}$  to  $138 \text{ cm}^{-2} \text{ atm}^{-1}$  (ref. 17) with an average of 125 to  $127 \text{ cm}^{-2} \text{ atm}^{-1}$ . Measurements of  $S_{02}$  range from 2.0 to  $2.8 \text{ cm}^{-2} \text{ atm}^{-1}$ . Since  $A \propto S$ , one can quickly adjust  $A$  if a different value of  $S$  is preferred.

The next problem is choosing the proper temperature to use in calculating the level populations. The rotational energies come into equilibrium very rapidly with the kinetic energies of the most abundant species, which are the neutral atoms and molecules. However, the cross sections for excitation of the vibrational levels are much smaller than the cross sections for excitation of rotational levels and one must compare in detail the excitation rates with the radiative depopulation rates.

A vibrational level of a molecule can be excited by radiative absorption, by radiative cascade, or by collisional excitation. The radiative absorption rate is given by  $B_{lu} \int J_\nu \phi_\nu d\nu$  where  $J_\nu$  is the mean intensity. Since  $B_{lu} = (c^2/2h\nu^3)A_{ul}$  for a vibration-rotation band, the radiative absorption rate due to the earth,  $R_\oplus$  is given by

$$R_\oplus(l,u) = \frac{1}{2} \int B_\nu^\oplus \phi_\nu d\nu B_{lu} \approx \frac{1}{2} B_\nu^\oplus B_{lu}$$

$$= \frac{(1/2)A_{ul}}{\exp(h\nu/kT_\oplus) - 1}$$

$B_\nu^\oplus$  is the Planck function at the temperature of the earth,  $T_\oplus$ . The radiative absorption rate for the sun,  $R_\odot$ , is given by

$$R_\odot(l,u) = \frac{\Omega_\odot}{4\pi} \frac{A_{ul}}{\exp(h\nu/kT_\odot) - 1}$$

where  $\Omega_\odot = 6.800 \times 10^{-5}$  ster and  $T_\odot \approx 5850^\circ$  K at  $5\mu$  (ref. 18). Radiative cascade occurs when a higher vibrational level is excited (by radiation from the sun) and the level decays by cascade instead of returning directly to the ground state. This is important for vibrational levels because  $A_{\Delta v=1} \gg A_{\Delta v=2} \gg A_{\Delta v=3}$ . For level  $v = 1$  the excitation rate from radiative cascade through  $v = 2$  is given by

$$R_F \approx \frac{A_{21}}{A_{21} + A_{20}} [R_\oplus(0,2) + R_\odot(0,2)] \approx R_\odot(0,2)$$

There are two kinds of collisional excitation: (1) translation-vibration ( $T-V$ ), where the kinetic energy of the colliding molecule goes into vibrational energy; and (2) vibration-vibration ( $V-V$ ) where the vibrational energy of the colliding molecule is transferred to the other molecule. The second reaction is strongly resonant for molecules with similar vibrational energy levels. The reaction rates are usually expressed for collisional de-excitation for  $T-V$  and in the exothermic direction for  $V-V$ ; that is,

$$R_{\text{deex}}^{(T-V)} = k_{\text{deex}}^{(T)} N_{\text{NO}} N_{\text{coll}}$$

and

$$R_{\text{ex}}^{(V-V)} = k_{\text{exo}}^{(T)} N_{\text{NO}} \frac{N_{\text{coll}}(v=1)}{N_{\text{coll}}(\text{total})}$$

or

$$R_{\text{deex}}^{(V-V)} = k_{\text{exo}} \frac{N_{\text{NO}}(v=1)}{N_{\text{NO}}(\text{total})} N_{\text{coll}}$$

where  $N_{\text{coll}}$  is the number density of the colliding molecule (or atom, for  $T-V$ ). For excitation, the rate coefficients  $k$  are related by  $k_{\text{ex}} = k_{\text{deex}} \exp(-h\nu/kT)$

and  $k_{\text{endo}} = k_{\text{exo}} \exp(-h\nu/kT)$ . The vibrational levels are deexcited by spontaneous emission, by stimulated emission, by absorption to higher levels, and by collisions. However, in all the cases considered here, the spontaneous emission rate is much larger than the stimulated emission, absorption, or collisional rates, which thus can be ignored. Then the population of the first vibrational level is given by

$$\frac{N_{v=1}}{N_{\text{tot}}} \approx \frac{N_{v=1}}{N_{v=0}} = \frac{R_{\oplus}(0,1) + R_{\odot}(0,1) + R_F + R_{\text{ex}}(T-V) + R_{\text{ex}}(V-V)}{A_{10}} = \exp\left(-\frac{h\nu}{kT_{\text{ex}}}\right)$$

where  $T_{\text{ex}}$  is the excitation temperature. (Similar equations hold for the higher vibrational levels. The intensity in the band is equal to the sum of the intensities from each vibration rotation transition with  $\Delta v = 1$ . However, the 1-0 transition is by far the strongest.) The resulting excitation temperature of NO ranges from 261° K at 400 km to 284° K at 200 km on the shaded side of the earth, and from 272° K to 289° K on the sunlit side of the earth for  $T = 1000^\circ$  K. For  $T = 2000^\circ$  K, the excitation temperature is only 4° K higher. The small variation in temperature shows that radiation from the earth dominates the excitation process. Thus the excitation temperature would be higher or lower if the temperature of the surface of the earth were higher or lower than average. Estimated vibration-rotation band intensities are given in table 7 for  $T = 1000^\circ$  K. Similar calculations of the excitation of NO have been done by Bauer *et al.* (ref. 19), Degges (ref. 20), and Kummeler and Bortner (ref. 21).

TABLE 7.— VIBRATION-ROTATION BANDS OF NO FOR  $T = 1000^\circ$  K

Altitude, km	Column density, cm <sup>-2</sup>	$I_{5.3\mu}$ , ergs cm <sup>-2</sup> sec <sup>-1</sup> sr <sup>-1</sup>	
		Night	Day
400	$3.5 \times 10^{10}$	$4.4 \times 10^{-7}$	$6.7 \times 10^{-7}$
350	$1.8 \times 10^{11}$	$2.4 \times 10^{-6}$	$3.5 \times 10^{-6}$
300	$9.3 \times 10^{11}$	$1.3 \times 10^{-5}$	$1.9 \times 10^{-5}$
250	$4.7 \times 10^{12}$	$8.3 \times 10^{-5}$	$1.1 \times 10^{-4}$
200	$2.4 \times 10^{13}$	$6.5 \times 10^{-4}$	$7.8 \times 10^{-4}$

The vibration rotation bands are spread out over a finite wavelength interval that increases with increasing rotational temperature. Carpenter and Franzosa (ref. 22) have calculated the absorption spectrum for the  $v = 0-1$  transition of NO for temperatures of 200° K to 4000° K. If the individual rotation lines are unsaturated, the absorption widths for the whole band should be similar to the band widths in emission. The half-power band widths and the tenth-power band widths have been estimated from the graphs of Carpenter and Franzosa (ref. 22) and are given in table 8 as  $\Delta\lambda/\lambda$ . The energy is quite spread out; narrow band spectrophotometry may not be bothered by the NO emission.

TABLE 8.— BAND WIDTHS FOR NO

	$T = 1000^\circ \text{ K}$	$T = 2000^\circ \text{ K}$
$\frac{\Delta\lambda_{(1/2)}}{\lambda}$		
Fundamental First overtone	0.10 .05	0.13 .06
$\frac{\Delta\lambda_{(1/10)}}{\lambda}$		
Fundamental First overtone	0.14 .07	0.19 .09

Since NO has a permanent dipole moment, it also has a rotational line spectrum in the far infrared. Hall and Dowling (ref. 23) have measured the wavelengths of the lines and the rotational constants of the molecule. The ground electronic state is the doublet  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$ ; the  $^2\Pi_{3/2}$  levels lie about  $121 \text{ cm}^{-1}$  above the  $^2\Pi_{1/2}$  levels. The rotational spectrum consists of transitions with  $\Delta J = 1$  within the  $^2\Pi_{1/2}$  level and with  $\Delta J = 1$  within the  $^2\Pi_{3/2}$  level. The number of molecules in an energy level  $J$  is given by

$$\frac{N_J}{N_{\text{tot}}} = \frac{Q_1}{Q} (2J + 1) \exp\left(-\frac{E_J}{kT}\right)$$

where the partition function  $Q$  equals  $kT/hcB$  if the energy levels are given by  $E_J = BJ(J + 1)$  and the effects of higher order vibrational levels on the energies  $E_J$  have been neglected.  $Q_1$  partitions the molecules into  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$

$$Q_1(^2\Pi_{1/2}) = \frac{1}{1 + \exp(-hcE_{121}/kT)}$$

$$Q_1(^2\Pi_{3/2}) = \frac{\exp(-hcE_{121}/kT)}{1 + \exp(-hcE_{121}/kT)}$$

where  $E_{121}$  is the energy separating the  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  levels ( $121 \text{ cm}^{-1}$ ). The value of the transition probabilities  $A_{J+1,J}$  were estimated from the dipole moment. Townes and Schawlow (ref. 24) give the rotational transition probability as

$$A_{J+1,J} = \frac{64\pi^4}{3h\lambda^3} \mu^2 \frac{J + 1}{2J + 3}$$



where  $\lambda$  is the wavelength of the line and  $\mu$  is the dipole moment of the molecule. Townes and Schawlow give the value for the dipole moment  $\mu = 0.16$  debyes for  $J = 0$ . However, the dipole moment is not constant with  $J$ , and particularly will vary if the higher order terms in the energy level equation  $E_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \dots$  are important. Since the higher order terms are important for NO, it is thus only an approximation to use  $\mu = 0.16$  debyes for all values of  $A_{J+1,J}$ .

The specific intensities of the NO rotational lines were calculated using the column densities for NO at 1000° K from table 8 and are given in table 9. Only a few lines are tabulated here since many of the lines have similar intensities because  $A/\lambda$  increases as  $N_{J+1}$  decreases. (At  $T = 1000^\circ$  K, the maximum level population occurs at  $J = 27/2$ , but the maximum emission occurs at  $J \sim 61/2$ .) At 1000° K the intensities are small, but they should be of the order of  $10^2$  larger for  $T = 2000^\circ$  K.

TABLE 9.— ROTATIONAL LINES OF NO AT 1000° K

Altitude, km	Intensity, ergs cm <sup>-2</sup> sec <sup>-1</sup> sr <sup>-1</sup>		
	109 $\mu$ [ <sup>2</sup> $\Pi_{1/2}$ , $J = 55/2 - 53/2$ ]	107 $\mu$ [ <sup>2</sup> $\Pi_{3/2}$ , $J = 55/2 - 53/2$ ]	82.4 $\mu$ [ <sup>2</sup> $\Pi_{1/2}$ , $J = 73/2 - 71/2$ ]
400	$1.8 \times 10^{-9}$	$1.5 \times 10^{-9}$	$1.6 \times 10^{-9}$
350	$9.2 \times 10^{-9}$	$7.5 \times 10^{-9}$	$8.3 \times 10^{-9}$
300	$4.7 \times 10^{-8}$	$3.8 \times 10^{-8}$	$4.3 \times 10^{-8}$
250	$1.0 \times 10^{-7}$	$8.5 \times 10^{-8}$	$9.4 \times 10^{-8}$
200	$8.7 \times 10^{-7}$	$7.9 \times 10^{-7}$	$7.4 \times 10^{-7}$

#### CO and CO<sub>2</sub>

Theoretical models of the abundances of CO and CO<sub>2</sub> have been calculated up to 200 km by Hays and Olivero (ref. 25) and up to 160 km by Hunt (ref. 26). The abundances below these altitudes are determined by diffusion and by the dissociation of CO<sub>2</sub> to CO. Since CO<sub>2</sub> is such a heavy molecule, its abundance falls off more rapidly than CO with increasing altitude. At 110 km both models give the density of CO<sub>2</sub> between  $3 \times 10^8$  and  $5 \times 10^8$  molecules/cm<sup>3</sup> and CO an order of magnitude less, but at about 160 km, the abundances of CO and CO<sub>2</sub> are equal. Densities and column densities were estimated for higher altitudes under the assumption of pure diffusive mixing. The molecule CO is very stable against ionization or dissociation, and diffusion should be accurate at high altitudes. Since CO has the same mass as N<sub>2</sub>, under diffusion it should scale as N<sub>2</sub>. The ratio of the CO abundance from Hunt's model (ref. 25) to the abundance of N<sub>2</sub> for  $T = 1000^\circ$  K increases from  $2.6 \times 10^{-5}$  at 110 km to  $8.5 \times 10^{-5}$  at 160 km because diffusion is not yet dominant at these altitudes. However, above these altitudes eventually diffusion dominates, and it was assumed that the column density of CO is equal to  $8.5 \times 10^{-5}$  times the column density of N<sub>2</sub> (table 4).

The vibration-rotation spectrum of CO consists of a fundamental band at  $4.67\mu$  and overtones at  $2.35\mu$  and shorter wavelengths. The collisional excitation rates for CO and CO<sub>2</sub> have been intensively studied because of the use of the molecules in lasers; the values used here came from the review by Taylor (ref. 27). At  $T = 1000^\circ \text{ K}$ , collisional excitation is relatively unimportant compared to radiation, and the excitation temperature of the upper vibrational level of the  $4.67\mu$  transition of CO ranges from  $291^\circ \text{ K}$  at 400 km to  $297^\circ \text{ K}$  at 200 km for molecules in the sun and from  $264^\circ \text{ K}$  to  $277^\circ \text{ K}$  for molecules shaded from the sun. However, at  $T = 2000^\circ \text{ K}$  the excitation temperature of CO ranges from  $320^\circ \text{ K}$  at 400 km to  $395^\circ \text{ K}$  at 200 km in the sun and from  $311^\circ \text{ K}$  to  $393^\circ \text{ K}$  in the shade. The intensities of the  $4.67\mu$  vibration-rotation fundamental of CO are given in table 10 for  $T = 1000^\circ \text{ K}$ . For higher temperatures, the intensities should be increased proportionally to the increased column density of N<sub>2</sub> times the increased population from the higher excitation temperature.

TABLE 10.— INTENSITIES FROM CO AT  $T = 1000^\circ \text{ K}$

Altitude, km	Intensity, ergs cm <sup>-2</sup> sec <sup>-1</sup> sr <sup>-1</sup>	
	4.67 $\mu$ (night)	4.67 $\mu$ (day)
400	$1.2 \times 10^{-8}$	$3.5 \times 10^{-8}$
350	$5.1 \times 10^{-8}$	$1.5 \times 10^{-7}$
300	$2.5 \times 10^{-7}$	$6.8 \times 10^{-7}$
250	$1.3 \times 10^{-6}$	$3.5 \times 10^{-6}$
200	$9.7 \times 10^{-6}$	$2.1 \times 10^{-5}$

The pure rotational lines of CO are fairly weak because of the small dipole moment (0.112 debyes). At  $T = 1000^\circ \text{ K}$ , the strongest line is at  $87\mu$ . Its intensity is about  $3.8 \times 10^{-10}$  ergs cm<sup>-2</sup> sec<sup>-1</sup> sr<sup>-1</sup>. At  $T = 2000^\circ \text{ K}$ , the strongest line is at  $63\mu$  and has an intensity of about  $3.6 \times 10^{-8}$  ergs cm<sup>-2</sup> sec<sup>-1</sup> sr<sup>-1</sup>. The total intensity of the CO rotation lines is almost two orders of magnitude less than the intensity of the NO rotation lines.

CO<sub>2</sub> has no pure rotational lines but it has many vibration rotation bands, the strongest of which are the  $\nu_2$  fundamental at  $15\mu$  and the  $\nu_3$  fundamental at  $4.26\mu$ . At  $T = 1000^\circ \text{ K}$ , collisional excitation of the  $15\mu$  band is negligible ( $T_{\text{ex}} = 198^\circ \text{ K}$ ) but at  $T = 2000^\circ \text{ K}$  the excitation temperature increases to  $232^\circ \text{ K}$  at 200 km. Radiative excitation from the sun is negligible. However, at  $4.26\mu$ , radiative excitation from the sun is most important. In the sunlight, the excitation temperature ranges from  $297^\circ \text{ K}$  at 400 km to  $301^\circ \text{ K}$  at 200 km; in the shade, however, the excitation temperature ranges from  $228^\circ \text{ K}$  at 400 km to  $260^\circ \text{ K}$  at 200 km. The intensities, given in table 11, are still very small because of the small column densities.

TABLE 11.— INTENSITIES FROM CO<sub>2</sub> AT  $T = 1000^\circ \text{ K}$ 

Altitude, km	Column density, $\text{cm}^{-2}$	Intensity, $\text{ergs cm}^{-2} \text{ sec}^{-1} \text{ sr}^{-1}$		
		4.26 $\mu$ (night)	4.26 $\mu$ (day)	15 $\mu$
400	$3.4 \times 10^2$	$1.2 \times 10^{-15}$	$4.3 \times 10^{-14}$	$8.8 \times 10^{-14}$
350	$3.7 \times 10^3$	$1.3 \times 10^{-14}$	$4.7 \times 10^{-13}$	$9.6 \times 10^{-13}$
300	$4.0 \times 10^4$	$1.7 \times 10^{-13}$	$5.1 \times 10^{-12}$	$1.0 \times 10^{-11}$
250	$4.4 \times 10^5$	$3.0 \times 10^{-12}$	$5.7 \times 10^{-11}$	$1.1 \times 10^{-10}$
200	$4.8 \times 10^6$	$1.1 \times 10^{-10}$	$7.0 \times 10^{-10}$	$1.2 \times 10^{-9}$

Ions ( $\text{O}^+$ ,  $\text{N}^+$ ,  $\text{O}^{++}$ ,  $\text{N}_2^+$ ,  $\text{O}_2^+$ ,  $\text{NO}^+$ )

Ionic densities are determined by diffusive equilibrium only at high altitudes, and are determined by photoionization and chemical reactions with ions and neutrals at lower altitudes. (The transition region is between 300 km and 500 km, depending on the density.) The ionic densities have been measured by ion mass spectrometers on various rocket and satellite flights. Unfortunately, the published densities above 300 km were all measured during quiet sun years, when  $T$  is less than average  $T = 1000^\circ \text{ K}$  and the emitted intensities are less than average. Holmes *et al.* (ref. 28) measured the ion densities on a day flight ( $T \sim 750^\circ \text{ K}$ ) and a night flight ( $T \sim 650^\circ \text{ K}$ ) in 1963. Brinton *et al.* (ref. 29) measured the ionic densities on a day flight in 1966 ( $T \sim 850^\circ \text{ K}$ ). Hoffman *et al.* (ref. 30) also measured the ion densities on a day flight in 1966 ( $T = 940^\circ \text{ K}$ ). This rocket flight coincided with the pass of the Explorer 31 satellite at 970 km, on which there were experiments that measured the kinetic temperature of the ions as  $2100^\circ \text{ K}$  and the electron temperature as  $3650^\circ \text{ K}$  and  $3700^\circ \text{ K}$ . The ionic column densities from the measurements with the largest gas temperature (Hoffman *et al.*, ref. 30) are given in table 12.

TABLE 12.— OBSERVED IONIC COLUMN DENSITIES AT  $T = 940^\circ \text{ K}$ 

Altitude, km	$\text{O}^+$ ions/ $\text{cm}^2$	$\text{N}^+$ ions/ $\text{cm}^2$	$\text{NO}^+$ ions/ $\text{cm}^2$	$\text{N}_2^+$ ions/ $\text{cm}^2$	$\text{O}_2^+$ ions/ $\text{cm}^2$	$\text{O}^{++}$ ions/ $\text{cm}^2$
400	$3.2 \times 10^{12}$	$1.4 \times 10^{11}$	$1.1 \times 10^{10}$	$1.1 \times 10^{10}$	$8.5 \times 10^9$	$5.5 \times 10^9$
350	$4.2 \times 10^{12}$	$1.7 \times 10^{11}$	$2.2 \times 10^{10}$	$2.1 \times 10^{10}$	$1.3 \times 10^{10}$	$5.9 \times 10^9$
300	$5.5 \times 10^{12}$	$1.9 \times 10^{11}$	$6.7 \times 10^{10}$	$4.2 \times 10^{10}$	$2.5 \times 10^{10}$	$6.3 \times 10^9$
250	$7.3 \times 10^{12}$	$2.1 \times 10^{11}$	$2.9 \times 10^{11}$	$8.4 \times 10^{10}$	$1.1 \times 10^{11}$	$6.7 \times 10^9$
200	$8.3 \times 10^{12}$	$2.1 \times 10^{11}$	$1.0 \times 10^{12}$	$1.5 \times 10^{11}$	$4.6 \times 10^{11}$	$7.0 \times 10^9$

Of the above ions,  $\text{O}_2^+$  and  $\text{N}_2^+$  are homonuclear and have no rotational lines or vibration rotation bands in the infrared. The ion  $\text{O}^+$  has a line at  $505\mu$ , but it is a transition between levels that are 3.3 eV above the ground state. With this small level population and its small transition probability

Garstang, ref. 5), the line should be no stronger than  $3 \times 10^{-14}$  ergs  $\text{cm}^{-2} \text{sec}^{-1}$  at 250 km, which is very weak indeed.

The ions  $\text{N}^+$  and  $\text{O}^{++}$  are  $2p^2$  configurations with  $^3P$  ground terms. The lines of  $\text{N}^+$  are at  $203.7\mu$  ( $^3P_0 - ^3P_1$ ) and  $121.7\mu$  ( $^3P_1 - ^3P_2$ ) and the lines of  $\text{O}^{++}$  are at  $88.18\mu$  ( $^3P_0 - ^3P_1$ ) and  $51.71\mu$  ( $^3P_1 - ^3P_2$ ). The level populations are given by the Boltzmann equation with the temperature equal to the temperature of the electrons since the cross sections for collisional excitation of  $\text{O}^{++}$  and  $\text{N}^+$  by electrons are sufficiently large. With the use of the transition probabilities from Garstang (ref. 5) and the column densities from table 9, the intensities for  $T = 940^\circ \text{K}$  are given in table 13.

TABLE 13.— INTENSITIES FOR  $\text{N}^+$  AND  $\text{O}^{++}$  AT  $T = 940^\circ \text{K}$

Altitude, km	Intensity, ergs $\text{cm}^{-2} \text{sec}^{-1} \text{sr}^{-1}$			
	[N II] $121.7\mu$	[N II] $203.7\mu$	[O III] $51.71\mu$	[O III] $88.18\mu$
400	$7.7 \times 10^{-10}$	$7.9 \times 10^{-11}$	$8.9 \times 10^{-10}$	$8.9 \times 10^{-11}$
350	$9.0 \times 10^{-10}$	$9.3 \times 10^{-11}$	$9.5 \times 10^{-10}$	$9.5 \times 10^{-11}$
300	$1.0 \times 10^{-9}$	$1.0 \times 10^{-10}$	$1.0 \times 10^{-9}$	$1.0 \times 10^{-10}$
250	$1.1 \times 10^{-9}$	$1.1 \times 10^{-10}$	$1.1 \times 10^{-9}$	$1.1 \times 10^{-10}$
200	$1.1 \times 10^{-9}$	$1.2 \times 10^{-10}$	$1.1 \times 10^{-9}$	$1.1 \times 10^{-10}$

The line strengths for  $\text{NO}^+$  have not been measured in the laboratory because  $\text{NO}^+$  is so reactive. However, Billingsley (ref. 31) has calculated Einstein coefficients for the vibration-rotation fundamental ( $4.27\mu$ ) and first overtone ( $2.15\mu$ ) and the dipole moment as a function of vibrational level.

Line  $\text{NO}$ ,  $\text{NO}^+$  is infrared-active and radiates in its vibration rotation transactions when it is excited. The main mechanism for excitation of the vibrational levels of  $\text{NO}^+$  is the radiation from the earth at night and the earth plus the sun in the daytime. The second mechanism is collisional excitation. Since the vibrational energy of  $\text{NO}^+$  is within  $18 \text{ cm}^{-1}$  of the energy of  $\text{N}_2$ , the cross section for interchange of vibrational energy with  $\text{N}_2$  is large. The molecule  $\text{N}_2$  is infrared inactive and its vibrational temperature should exceed the gas kinetic temperature. The reaction rate for collisional excitation by  $\text{N}_2$  was estimated from other resonant and near resonant reactions with  $\text{N}_2$ . The resulting vibrational temperatures for  $\text{NO}^+$  vary between  $220^\circ \text{K}$  at night at 400 km altitude where collisions are negligible, to  $290^\circ \text{K}$  during the day at 400 km. Collisional excitations bring the excitation temperature to over  $360^\circ \text{K}$  at 200 km when  $T = 2000^\circ \text{K}$ . The average vibrational temperature is around  $300^\circ \text{K}$ .  $\text{NO}^+$  vibration rotation intensities are given in table 14 for  $T = 940^\circ \text{K}$ . The column densities needed for the calculations in table 14 were taken from table 12. However, it should be noted here that the densities of  $\text{NO}^+$  found by Goldberg and Blumle (ref. 32) for  $T \sim 1100^\circ \text{K}$  are less than the densities of  $\text{NO}^+$  given by Hoffman *et al.* (ref. 30) at  $T = 940^\circ \text{K}$  for altitudes less than 300 km. For lower gas temperatures, the measured density of  $\text{NO}^+$  is much less.

TABLE 14.— VIBRATION-ROTATION FUNDAMENTAL OF  $\text{NO}^+$   
AT  $\lambda = 4.27\mu$ ;  $T = 940^\circ \text{ K}$

Altitude, km	Intensity, $\text{ergs cm}^{-2} \text{ sec}^{-1} \text{ sr}^{-1}$	
	Night	Day
400	$1.3 \times 10^{-9}$	$5.0 \times 10^{-8}$
350	$2.9 \times 10^{-9}$	$1.0 \times 10^{-7}$
300	$1.5 \times 10^{-8}$	$3.1 \times 10^{-7}$
250	$2.6 \times 10^{-7}$	$1.5 \times 10^{-6}$
200	$4.0 \times 10^{-6}$	$8.2 \times 10^{-6}$

The intensities of  $\text{NO}^+$  may be higher than the values in table 14 by as much as a factor of 200. When a molecule is formed, most of the energy of the reaction goes into vibrational excitation of the molecule. The rate of formation of  $\text{NO}^+$  is about  $10^2$  larger than the rate of excitation of the first vibrational level from collisions and radiative excitations. Consequently, the rate of spontaneous emission will be larger than that given in table 14 depending on the fraction of  $\text{NO}^+$  molecules formed in an excited state. (The rate of formation of NO is not fast enough for this excitation mechanism to be important.)

The intensity of  $\text{NO}^+$  will be much stronger for higher temperatures. It is thought that the most important reaction for forming  $\text{NO}^+$  is  $\text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N}$ , with  $\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$  almost as important. If the abundance of  $\text{NO}^+$  scales as  $\text{N}_2$ , then the intensity of the  $4.27\mu$  vibration-rotation fundamental at 350 km should be 50 percent larger at  $T = 1000^\circ \text{ K}$  and larger by a factor of 50 for  $T = 2000^\circ \text{ K}$ . Actually, the density of  $\text{NO}^+$  increases faster with temperature than the density of  $\text{N}_2$ . The reason is that the cross section for the reaction  $\text{O}^+ + \text{N}_2 \rightarrow \text{NO} + \text{N}$  increases with increasing vibrational temperature of  $\text{N}_2$ . Thus at higher gas temperatures, more  $\text{NO}^+$  is formed per  $\text{N}_2$  molecule.

The rotational line strengths of  $\text{NO}^+$  were calculated using the gas temperature because the rotational energies are coupled much more strongly to the translational energies. At  $T = 1000^\circ \text{ K}$ , the strongest line is at  $87\mu$  and has an intensity of  $1.3 \times 10^{-8} \text{ ergs cm}^{-2} \text{ sec}^{-1} \text{ sr}^{-1}$  at 350 km. However, at  $T = 2000^\circ \text{ K}$ , the strongest line would be at  $60\mu$  and would have an intensity of about  $1.3 \times 10^{-6} \text{ ergs cm}^{-2} \text{ sec}^{-1} \text{ sr}^{-1}$ .

#### AN EXAMPLE

It is necessary to know the infrared fluxes from the upper atmosphere when planning infrared astronomical telescopes to be carried on satellites such as the space shuttle. It is currently planned that the space shuttle infrared telescope will be 1 m in diameter and a typical detector will have a 1-arc-min field of view. The most interesting quantity is the flux of

energy  $E$  entering the detector. For a perfectly efficient system, this is given by

$$E = IA\Omega$$

where  $A$  is the area of the aperture of the telescope and  $\Omega$  is the solid angle of the beam. A 1-m telescope has  $A = 0.785 \times 10^4 \text{ cm}^2$ . A beam of 1 arc min<sup>2</sup> has  $\Omega = 0.846 \times 10^{-7} \text{ sr}$ . Thus a 1-m telescope with a beam of 1 arc min<sup>2</sup> will measure  $I \times 0.6646 \times 10^{-10} \text{ W}$  if  $I$  is in ergs cm<sup>-2</sup> sec<sup>-1</sup> sr<sup>-1</sup>.

The noise due to the photon fluctuations of the radiation can be expressed as  $NEP = \sqrt{E \times E_p}$  where  $E_p$  is the energy per photon =  $h\nu$ . For the above 1-m telescope,  $NEP = \sqrt{(1.320 \times 10^{-29} I / \lambda_\mu)} \text{ W/Hz}^{1/2}$  where  $I$  is in ergs cm<sup>-2</sup> sec<sup>-1</sup> ster<sup>-1</sup> and  $\lambda_\mu$  is the wavelength in microns.

A summary of these calculations for a 1-m telescope with a beam of one arc minute at 350 km when  $T = 1000^\circ \text{ K}$  on the day side of the earth is given in table 15. The NO and NO<sup>+</sup> rotation lines are summed into 10 $\mu$  bands.

TABLE 15.— RADIATION FROM THE ATMOSPHERE ENTERING A 1-m TELESCOPE WITH A 1-arc-min FIELD OF VIEW

$\lambda, \mu$	Watts into the detector	$NEP, \text{ W/Hz}^{-1/2}$
[OI] 63.1	$8.0 \times 10^{-15}$	$5.0 \times 10^{-18}$
[OI] 147	$2.0 \times 10^{-16}$	$5.2 \times 10^{-19}$
[N II] 121.7	$6.0 \times 10^{-20}$	$9.9 \times 10^{-21}$
[OIII] 51.71	$6.3 \times 10^{-20}$	$1.6 \times 10^{-20}$
O <sub>2</sub> 77.8	$5.3 \times 10^{-22}$	$1.2 \times 10^{-21}$
CO 4.7	$1.0 \times 10^{-17}$	$6.5 \times 10^{-19}$
NO 5.3	$2.3 \times 10^{-16}$	$2.9 \times 10^{-18}$
NO <sup>+</sup> 4.3	$1.0 \times 10^{-17}$	$7.0 \times 10^{-19}$
CO + NO + NO <sup>+</sup> 60-70	$8.0 \times 10^{-18}$	$1.6 \times 10^{-19}$
CO + NO + NO <sup>+</sup> 70-80	$1.0 \times 10^{-17}$	$1.6 \times 10^{-19}$
CO + NO + NO <sup>+</sup> 80-90	$1.0 \times 10^{-17}$	$1.5 \times 10^{-19}$

The line strengths will increase by factors of 2 to 5 for every 50 km that one goes down in altitude, and will increase by factors of 5 to 10 as the temperature of the gas is doubled. One must remember that  $T = 1000^\circ \text{ K}$  is only an *average* temperature, and that 1 percent of the time the temperature is over  $1900^\circ \text{ K}$ . In addition, the path length and the column density increase as one looks away from the zenith. Except for very large zenith angles  $\theta$ , the column density and the path length increase as  $\sec \theta$ ; this is a factor of 2 for  $\theta = 60^\circ$ .

## SUMMARY OF RESULTS

Infrared radiation from atoms and molecules in the earth's upper atmosphere has been calculated for zenith lines-of-sight at altitudes from 200 km to

400 km. The infrared spectra at each of five altitudes are plotted in figures 1(a)-(e). Because of the great uncertainty in extrapolating the abundances, only spectra for the average condition  $T = 1000^\circ \text{ K}$  have been plotted. However, rough estimates can be made of the intensities for  $T = 2000^\circ \text{ K}$ . The intensity of the  $\text{NO}^+$  4.3- $\mu$  band at 300 km is increased by a factor of 25 on the sunlit side and by a factor of 200 on the dark side (i.e., collisional excitation now dominates over radiative excitation), the NO band at 5.3 $\mu$  is increased by a factor of 25, and the CO band at 4.7 $\mu$  is increased by a factor of 70 on the sunlit side and by a factor of 150 on the dark side. The energy in the  $\text{NO} + \text{NO}^+ + \text{CO}$  pure rotation lines is increased by a factor of 50 and the maximum emission is in the 50 $\mu$ -60 $\mu$  band instead of 80 $\mu$ -90 $\mu$  band.

Because accurate abundances and excitation cross sections were not available for many of the cases considered, the predictions of infrared intensity are only estimates. For neutral atomic oxygen, the intensities for all temperatures are probably good to 50 percent, but for the ions and molecules the abundances and column densities are much less certain. Computations of the NO and CO abundances have only been done for average temperatures. At higher temperatures the increased density will make reactions of formation and destruction more likely, and thus make the abundance of NO and CO scale differently from that given by pure diffusion (i.e., like  $\text{N}_2$ ). Similarly, higher temperatures are caused by increased solar UV flux, which in turn causes increased ionization, but higher densities bring about increased recombination. For the vibration-rotation bands of  $\text{NO}^+$  there is additional uncertainty because the band strengths have not been measured in the laboratory. Moreover, the collisional excitation rates for all the molecules are quite uncertain. The final uncertainties (95 percent confidence) for  $T = 1000^\circ \text{ K}$  might be as high as one order of magnitude and minus one-half order of magnitude for the  $\text{NO}^+$  vibration-rotation band, plus and minus one-half order of magnitude for the NO and CO vibration-rotation bands, and plus one-half order of magnitude and minus one order of magnitude for the pure rotation lines. The uncertainties at  $T = 2000^\circ \text{ K}$  are one-half an order of magnitude larger in the molecular lines.

Ames Research Center

National Aeronautics and Space Administration

Moffett Field, Calif., 94035, Oct. 23, 1975

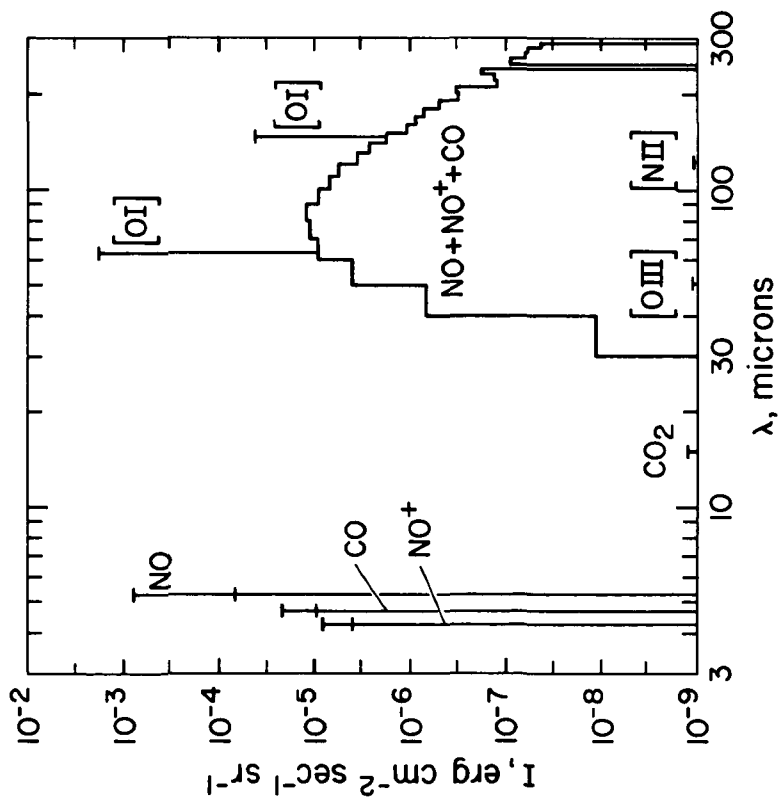
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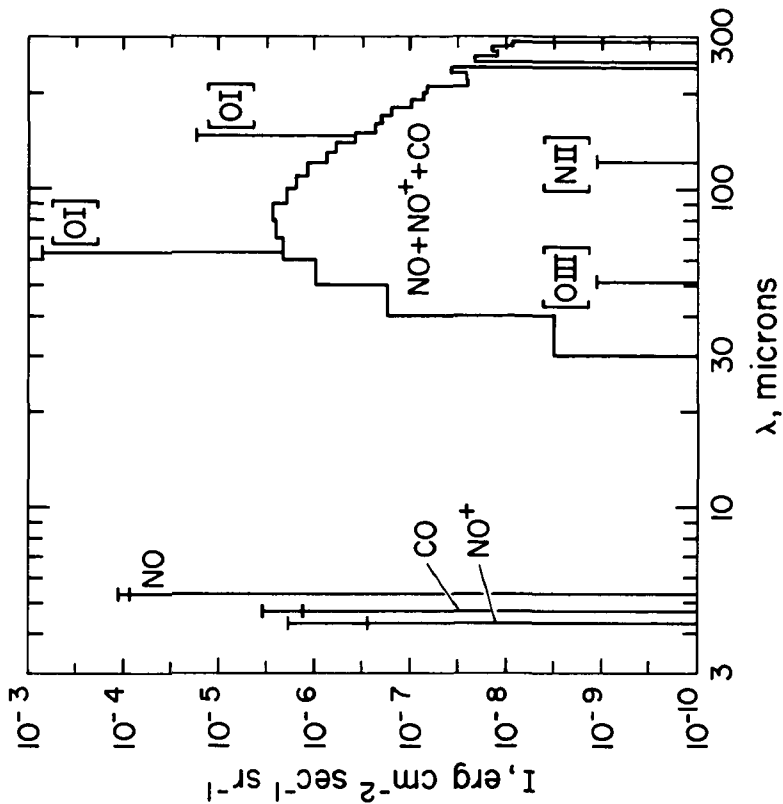


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(a) Altitude  $R = 200$  km.



(b) Altitude  $R = 250$  km.

Figure 1.— The infrared emission from the upper atmosphere of the earth at zenith line of sight is plotted as a function of wavelength. The column densities for the average kinetic gas temperature  $T = 1000^\circ$  K were used. For the  $\text{NO}^+$ , CO, and NO vibration-rotation bands, the intensity on the sunlit side of the earth is given by the upper tick mark and the intensity on the dark side of the earth is given by the lower tick mark. The NO,  $\text{NO}^+$ , and CO rotation lines have been summed into  $10\mu$ -wide bands; for these bands the units are then  $\text{erg cm}^{-2} \text{ sec}^{-1} \text{ sr}^{-1} 10\mu^{-1}$ .

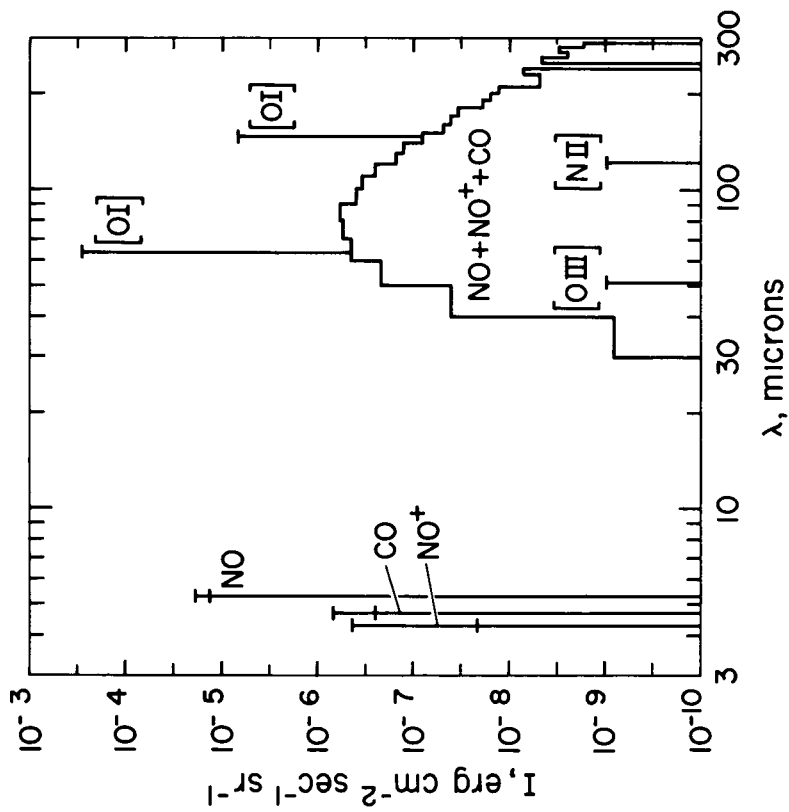
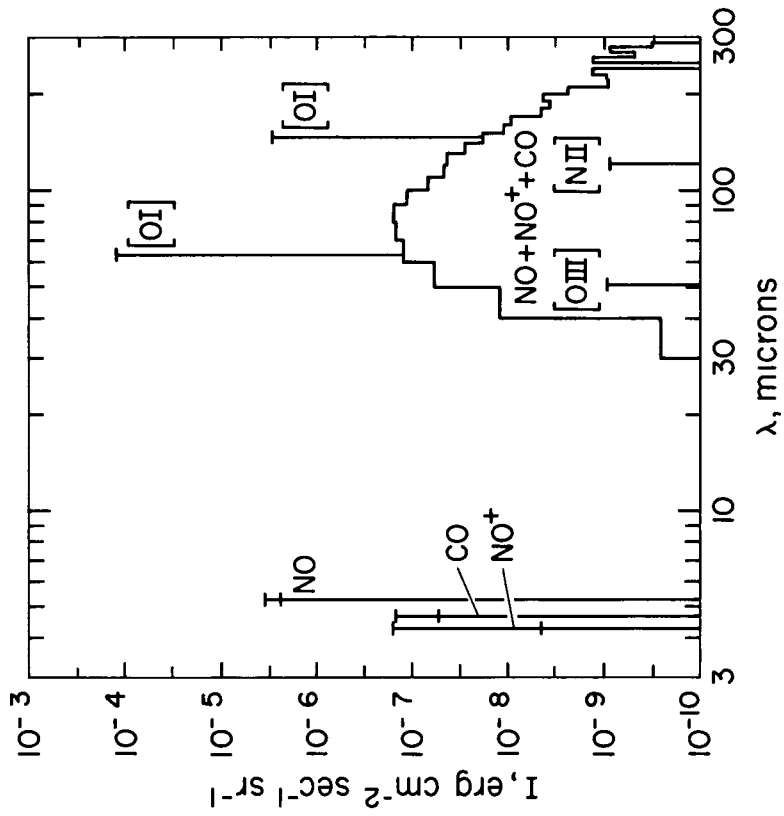
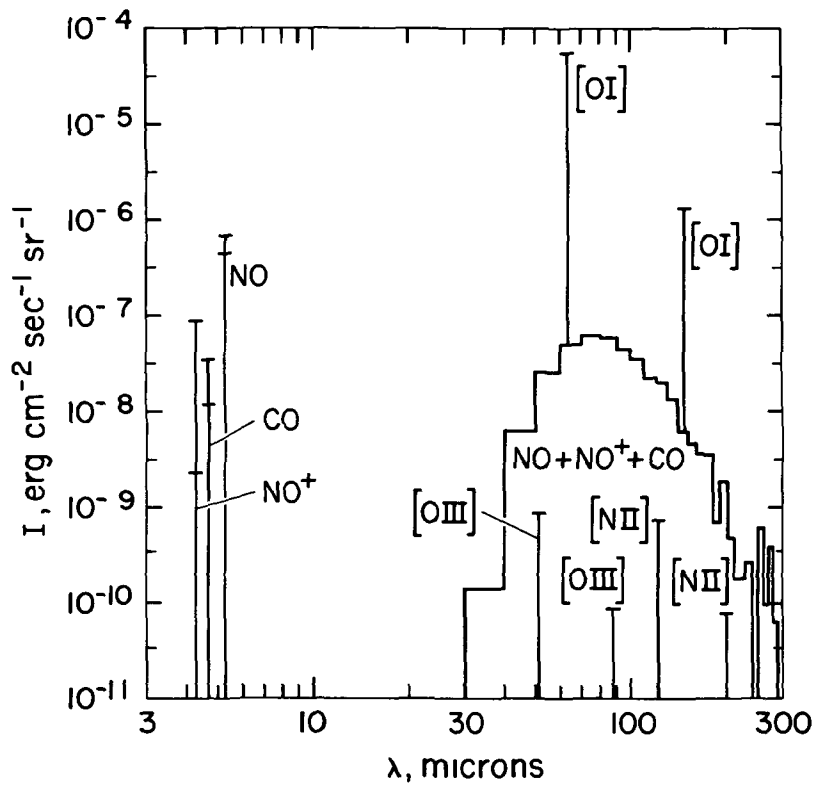
(c) Altitude  $R = 300$  km.(d) Altitude  $R = 350$  km.

Figure 1.— Continued.



(e) Altitude  $R = 400$  km.

Figure 1.— Concluded.



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